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A New Colorimetric Method for the Determination of a Small Amount of Cesium*

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A new method using $HBiI_4$ reagent has been established for the colorimetric determination of a small amount of cesium. By this method, 10 to 45 μg of cesium can be determined in the presence of less than 4 mg. of potassium and rubidium.

INTRODUCTION

In order to determine a microgram order of cesium in a large amount of rubidium, it has been necessary to depend upon the spectrographic method since the chemical separation of cesium from the above-mentioned sample has been next to impossible. Moreover, it has been found that the identification limit of cesium using the visible spectral lines is 20 μg or so at the most and the intensity of the spectral lines are considerably affected by the presence of other elements. During the course of an investigation of the reaction between the $KBiI_4$ reagent and a small amount of cesium, a possible method for the determination of cesium in the above-mentioned sample has been found. The principle of the method is as follows: To the dried cesium sample, the $HBiI_4$ reagent is added and the resulting cesium salt, $Cs_3Bi_2I_9$ is washed with cold concentrated acetic acid. Then the precipitate is dissolved in dilute nitric acid and the amount of the cesium is indirectly found by the colorimetric determination of bismuth using dithizone-chloroform. This method owes its development to the following experimental facts.

1) The identification limit of cesium is 0.2μg when 0.03ml. of $HBiI_4$ reagent is added to a solid cesium sample.

2) Under the same procedure as the above mentioned one, even 0.5μg of cesium can be obtained as a red precipitate.

3) Similarly, 5 μg of cesium in 2 mg. of rubidium can be obtained as a red precipitate.

4) Apparently, the amount of the cesium salt obtained is proportional to the amount of the cesium.

5) In the quantitative semi-micro analysis of cesium, it has been reported that the amount of coprecipitated rubidium with a definite amount of cesium salt increases only gradually with a rapid increase in the amount of the accompanying rubidium in the sample.

6) The cesium salt in the presence of a large amount of potassium is ob-

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tained more easily than that in the case with rubidium.

7) The cesium salt is less soluble in concentrated acetic acid than in water, and washing with concentrated acetic acid is easier than with water.

REAGENT AND APPARATUS

$HBiI_4$ reagent : 4 grams of purified bismuth trioxide was dissolved in hydroiodic acid which was obtained by passing hydrogen sulfide gas into 100 ml. of water containing 20 grams of purified iodine. The filtered solution was stored in a glass-stoppered bottle in a cold place avoiding light. It is good for about three months.

Dithizone-chloroform solution : 60 mg, of dithizone was dissolved in dilute ammonium hydroxide solution (1 : 200) and impurities were extracted with chloroform. The aqueous dithizone phase was filtered through a pledget of cotton inserted in the stem of a separatory funnel into another funnel. The filtrate was carefully acidified with metal-free hydrochloric acid (1 : 1) to precipitate dithizone, which was then reextracted with purified chloroform. The chloroform layer was filtered as before and diluted to 500 ml. with purified chloroform for future use.

Standerd bismuth solution : 100 p.p.m. of bismuth solution was prepared by using purified bismuth trioxide.

Rubidium nitrate : The rubidium nitrate was purified by the previously reported method. The cesium which might be minutely present in the rubidium nitrate, could not be identified with $HBiI_4$ reagent which is capable of detecting as little as 0.2 μg of cesium, Moreover, it was confirmed that there is no interference even in the determination of cesium in large amounts of rubidium. Rubidium nitrate solutions of 10, 100 and 1000 p.p.m. were prepared.

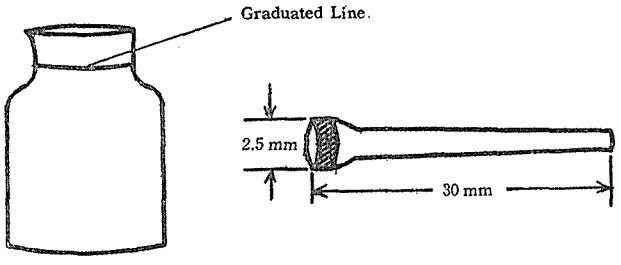
Cesium nitrate : Cesium nitrate solutions of 2, 5 and 10 p.p.m. were prepared.

Nitric acid : 1% and 3% solutions.

Concentrated ammonium hydroxide : Redistilled.

Potassium cyanide : Special grade reagent.

A Hitachi filter photometer Model EPO-A equipped with 1 cm. cells and filters of approximately 30 mμ band width was used for all photometric measure-



(A) (B)

Fig. 1. Glass apparatus.

ments.

A Beckman Model H-2 pH meter was utilized to measure the pH values. The glass apparatus shown in Fig. 1 was used. (A) is a graduated 10 ml. vessel and (B) a filter-stick with a sintered glass-filter-plate.

EXPERIMENT

(1) Absorption Curve of Bismuth Dithizonate[1]

According to the literature, the absorption curve of bismuth dithizonate is said to have its maximum peak at 490 to 505 mμ wave length. The author also found that the absorption curves of the bismuth dithizonates from which 10 and 20 μg of bismuth were extracted rspectively with chloroform-dithizone solution, showed their maximum absorption at 500 mμ. For the determination of bismuth dithizonate with a filter-photometer, "Filter C" was found to be appropriate because the concentration of bismuth and the absorbance are proportional with it.

(2) Procedure

A sample containing a small amount of cesium and additional elements such as rubidium and potassium is put in the vessel shown in Fig. 1 and evaporated to dryness on a steam-bath. After drying the residue in an air-bath at about 150°C for half an hour, it is cooled in a desiccator. Then, three drops (0,03~0.04 ml.) of $HBiI_4$ reagent which has been cooled in ice-water for more than an hour is added to the ice-cooled vessel and agitated so as to wet the vessel wall with reagent. As soon as the other salts accompanying the cesium—generally, potassium and rubidium salts-have dissolved, the precipitate is filtered through the filter-stick as shown in Fig. 1. This operation is generally done within four minutes after the addition of reagent and is satisfactory even in the presence of 4 mg. of potassium or rubidium. The precipitate is washed with 1 ml. of cold conc. acetic acid five to six times and treated with 3 ml. of 3% nitric acid. After heating it on a steam-bath for about 30 minutes, the filter-stick is washed with 1% hot nitric acid and the filtrate is put in the previous vessel. The solution is transferred into a separatory funnel and then, 20 ml. of potassium cyanide-ammonium hydroxide solution (10 g. KCN/*l* NH_4OH), 40 ml. of 1% nitric acid which has been treated with 8 ml. of dithizone-chloroform solution, and exactly 15 ml. of dithizone-chloroform solution are added to the solution. After shaking for about one minute, the chloroform layer is filtered through a filter paper and the absorbance is read in comparison with a blank solution.

(3) Results

a) Calibration curve : The calibration curve for cesium obtained by means of the above mentioned procedure is shown in Fig. 2. It was found that, in the absence of interfering ions, Beer's Law holds for 2.3 to 45 μg of cesium.

b) Determination of cesium in the presence of potassium : The results obtained in the presence of 10, 100, 200 and 400μg respectively of potassium are shown in Table 1. It is seen from the Table that up to 4000μg, potassium does

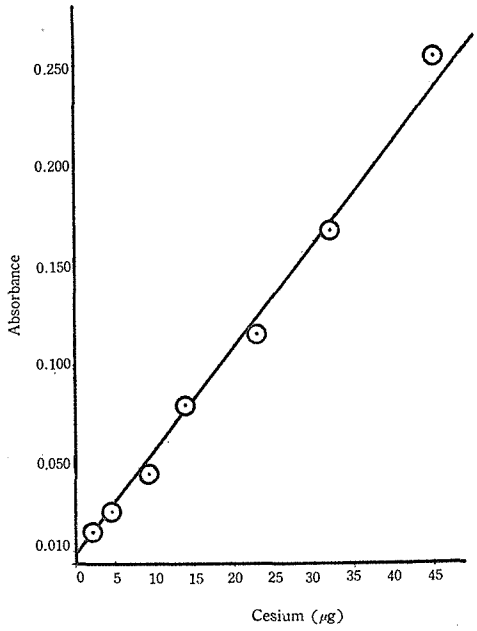


Fig. 2. Calibration curve for cesium.

Table 1. Determination of cesium in the presence of potassium.

K taken (μg.)	Cs taken (μg.)	Cs found (μg.)	Error (μg.)	K taken (μg.)	Cs taken (μg.)	Cs found (μg.)	Error (μg.)
10	2.5	2.3	−0.2	2000	2.5	2.0	−0.5
10	5	4.3	−0.7	〃	5	4.6	−0.4
10	10	11.5	+1.5	〃	10	8.7	−1.3
10	15	14.1	−0.9	〃	15	14.0	−1.0
10	25	24.7	−0.3	〃	25	26.3	+1.3
10	35	33.2	−1.8	〃	35	33.7	−1.3
10	45	46.4	+1.4	〃	45	47.1	+2.1
100	2.5	2.4	−0.1	4000	2.5	1.2	−1.3
100	5	4.6	−0.4	〃	5	2.6	−2.4
100	10	9.1	−0.9	〃	10	7.8	−2.2
100	15	13.8	−1.2	〃	15	14.1	−0.9
100	25	26.5	+1.5	〃	25	26.2	+1.2
100	35	34.8	−0.2	〃	35	33.6	−1.4
100	45	43.3	−1.7	〃	45	42.2	−2.8

not interfere with the determination of 10~45 μg of cesium, but in the presence of more than 2000μg potassium, determinations of cesium of less than 10 μg give negative errors owing to the salt effect.

c) Determination of cesium in the presence of rubidium : The results obtained in the presence of rubidium are shown in Table 2, and the relations between the absorbance and the amount of existing rubidium are given in Table 3 for various amounts of cesium.

Table 2. Determination of cesium in the presence of rubidium.

Cs taken (μg.)	Rb taken (μg.)	Cs found (μg.)	Error (μg.)	Cs taken (μg.)	Rb taken (μg.)	Cs found (μg.)	Error (μg.)
2.5	2.5	2.3	−0.3	2.5	10	2.8	+0.3
5	5	4.5	−0.5	5	15	5.0	±0.0
10	10	9.5	−0.5	10	20	9.5	−0.5
15	15	15.6	+0.6	15	30	16.8	+1.8
25	25	23.0	−2.0	25	50	30.3	+5.3
35	35	37.5	+2.5	35	70	44.0	+9.0
45	45	49.3	+4.3	45	90	very positive	

Table 3. Relations between rubidium and absorbance at various amounts of cesium.

Cs taken (μg.)	Rb taken (μg.)	Absorbance	Cs taken (μg.)	Rb taken (μg.)	Absorbance
2.3	0	0.016	2.5	2.5	0.015
4.6	0	0.026	5	5	0.026
9.2	0	0.045	10	10	0.052
13.8	0	0.079	15	15	0.082
23.0	0	0.115	25	25	0.121
32.0	0	0.168	35	35	0.197
45.0	0	0.255	45	45	0.298
2.5	10	0.017	2.5	50	0.013
5	15	0.027	5	50	0.021
10	20	0.052	10	50	0.057
15	30	0.088	15	50	0.093
25	50	0.159	25	100	0.150
35	70	0.245	35	100	0.230
45	90	0.364	45	100	0.383
10	500	0.053	10	750	0.051
15	500	0.105	15	750	0.097
25	500	0.158	25	750	0.169
35	500	0.233	35	750	0.255
45	500	0.398	45	750	0.413
10	1000	0.045	10	1500	0.041
15	1000	0.091	15	1500	0.082
25	1000	0.182	25	1500	0.193
35	1000	0.277	35	1500	0.293
45	1000	0.437	45	1500	0.456
10	2000	0.038	10	2500	0.035
15	2000	0.076	15	2500	0.081
25	2000	0.206	25	2500	0.217
35	2000	0.328	35	2500	0.355
45	2000	0.480	45	2500	0.496
10	3000	0.033	10	3500	0.032
15	3000	0.074	15	3500	0.081
25	3000	0.234	25	3500	0.241
35	3000	0.348	35	3500	0.356
45	3000	0.508	45	3500	0.522
10	4000	0.030			
15	4000	0.083			
25	4000	0.250			
35	4000	0.369			
45	4000	0.536			

As can be seen from Table 2, it is obvious that the calibration curve (Fig. 2) can be used when the amount of rubidium present is less than that of cesium but it cannot be used in the presence of an amount of rubidium greater than that of cesium, because the values for cesium involve large positive errors with increasing amounts of rubidium. These results correspond to those obtained

in the gravimetric analysis of semi-micro quantities of cesium.

However, as Table 3 indicates, the absorbances change only gradually with an increase of rubidium, and good results can be obtained if we adopt the following groups with regard to rubidium and use the portions of the calibration curve for these given ranges of rubidium: 0~X, X~X+500, X+500~×+1000, X+1000~X+1500 μg etc.—here X denotes the amount of rubidium equal to that of cesium contained in a sample.

As a preliminary experiment for the determination of cesium dissolved in sea-water, a measurement was made for samples containing 2000 μg of rubidium with 10, 20, 30 μg of cesium respectively. The total weight of rubidium and cesium as their dipicrylaminates (H_{Rb+Cs}) was determined. After removal of amine, the amount of cesium was determined by the above mentioned procedure using the calibration curve obtained in the presence of 2000 μg of rubidium. The results are shown in Table 4. According to the results, interference due

Table 4. Determination of cesium in the presence of a large amount of rubidium.

Exp. No.		1	2	3
Cs taken	(μg.)	10	20	30
Rb taken	(μg.)	2000	2000	2000
Hrb+Cs	(mg.)	12.10	12.23	12.35
Rb(≒Rb+Cs)	(mg.)	1.98	2.00	2.02
Absorbance		0.032	0.161	0.229
Cs found	(μg.)	9.2	21.8	27.3
Error	(μg.)	−0.8	+1.8	−2.7

to the presence of potassium and rubidium is almost analogous to the case of rubidium alone. Thus, a small amount of cesium in the presence of potassium or rubidium or both can be easily estimated without separating it ; We need only take into account the interference due to rubidium.

SUMMARY

There has previously been no report by which a microgram quantity of cesium in a large amount of rubidium can be determined colorimetrically, but a new method using $HBiI_4$ reagent has been established for the colorimetric determination of cesium in such a sample. By this method, 10~45 μg of cesium can be determined in the presence of potassium and rubidium less than 4 mg. by using several corrected calibration curves.

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